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An eleven-vertex deltahedron with hexacapped trigonal bipyramidal geometry†

C. W. Liu,*[a] Ping-Kuei Liao,[a] Ching-Shiang Fang,[a] Jean-Yves Saillard,*[b] Samia Kahlal[b] and Ju-Chun Wang[c]

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The first elemental cluster with hexacapped trigonal bipyramidal geometry is revealed in the luminescent undecanuclear silver complex which is stabilized by nine dithiocarbamate ligands and has an interstitial hydride. The hydride position within the Ag_{11} cage is confirmed by a DFT investigation.

Deltahedra are polyhedra containing exclusively triangular faces. Accordingly topologies of the two most commonly observed 11-vertex deltahedra are the octadecahedron (or edge-coalesced icosahedrons)[1] identified in $B_{11}H_{11}^{2-}$ and the compressed (or triflattened) pentacapped trigonal prism in E_{11}^{7-} (E = Ga, In , Tl) and $[Rh_5Ni_6(CO)_{21}H_x]^{3-}$ (Scheme 1).[2] The latter geometry is also known as the computed global minimum for Ge_{11}^{4+}.[2d] Despite variations of the degrees of vertices in these deltahedra, the total vertex connectivities of 54 keep the same. Herein we present a new topology for an 11-vertex deltahedron; that is the hexacapped trigonal bipyramid identified in the hydride endohedral Ag_{11} cluster supported by nine dialkyl dithiocarbamate (dtc) ligands.

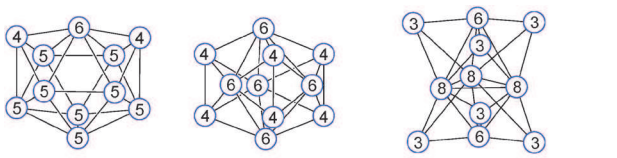
We are interested in exploring the chemistry of metal hydrides because these molecules are key intermediates in various catalytic reactions.[3] Despite a broad spectrum of transition metal hydrides has been thoroughly discussed, the silver hydrides have been much less explored until recently.

Thus a hydride on a silver cluster was proposed as a key step in both the dehydrogenation of alcohols to ketones and the C–C cross-coupling of secondary alcohols with primary alcohols, catalyzed by Al_2O_3-supported silver clusters.[4] Although the subvalent silver hydride clusters $(Ag_2H)^+$,[5] and $(Ag_4H)^+$,[6] have been identified in the gas phase, and small neutral and charged silver cluster hydrides (Ag_nH, n = 1–7) have been extensively studied by density functional methods,[7] surprisingly, a well-characterized silver-only hydrido complex was virtually unknown until hydride-encapsulated octanuclear silver clusters which displayed a tetracapped tetrahedral metallic skeleton and supported by six dichalcogenophosphate ligands ($E_2P(OR)_2^-$, E = S, Se),[8] were reported by this group.

Since there has been growing interest in silver cluster hydrides formed in silver-exchange zeolites,[9] it will be valuable to provide more silver hydrido clusters of defined geometry to model the above-mentioned catalytic reactions. Through this consideration, the hydrido silver cluster synthesis developed by this group is extended to utilize more accessible sulfur-donor ligands as cluster-stabilizing agents with the aim of isolating more silver hydrido clusters with different nuclearities. Thus dithiocarbamates (dtc), a well-known versatile class of monoanionic 1,1-dithio ligands which has been involved in the development of a wide range of coordination chemistry[10] and used as a capping agent for nanoparticle syntheses,[11] are chosen.

Herein we present the synthesis, structure, photophysical property, and DFT calculation on the new class of luminescent hydrido silver clusters, $[Ag_{11}(H)(S_2CNPr_2)_9](NO_3)$ **1**, which silver framework constitutes an unusual hydride-encapsulated, hexacapped trigonal bipyramid. To the best of our knowledge, *molecular geometry of a hexacapped trigonal bipyramid has never been identified in any clusters*.

The reaction of $Na(S_2CNPr_2)$ with $AgNO_3$ in the presence of $NaBH_4$ in a 9 : 11 : 1 molar ratio in MeCN at −20 °C for 3 h gives rise to clusters with a formula of $[Ag_{11}(H)(S_2CNPr_2)_9](NO_3)$ $\mathbf{1_H}$. A similar reaction carried out in the presence of $NaBD_4$ instead of $NaBH_4$ produces $[Ag_{11}(D)(S_2CNPr_2)_9](NO_3)$ $\mathbf{1_D}$. The ^1H NMR spectrum of compound $\mathbf{1_H}$ displays a set of chemical shifts corresponding to the propyl group at ambient temperature. In addition a broad peak centered at 7.50 ppm that integrates to *1H* relative to 36 methylene



(a) *Closo*-$B_{11}H_{11}^{2-}$ (b) In_{11}^{7-} (c) Hexacapped trigonal bipyramid

Scheme 1 11-vertex deltahedra.

[a] *Department of Chemistry, National Dong Hwa University, Hualien, Taiwan 97401, R.O.C. E-mail: chenwei@mail.ndhu.edu.tw; Fax: +866-3-863 3570; Tel: +886-3-863 3607*
[b] *UMR-CNRS, 6226 "Sciences Chimiques de Rennes", Université de Rennes 1, 35042 Rennes Cedex, France. E-mail: jean-yves.saillard@univ-rennes1.fr*
[c] *Department of Chemistry, Soochow University, Taipei, Taiwan 111, ROC*

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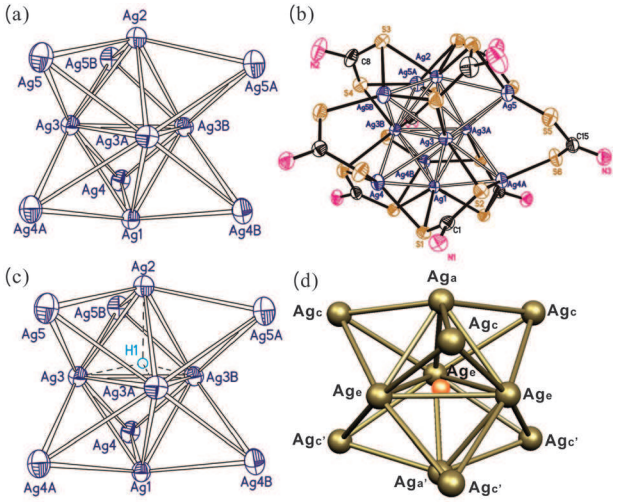

Fig. 1 (a) The thermal ellipsoid drawing of Ag_{11} skeleton. (b) The thermal ellipsoid drawing of cationic part of $\mathbf{1_H}$. Propyl groups and an entrapped hydride have been omitted for clarity. (c) A perspective view of the $Ag_{11}H$ core of $\mathbf{1_H}$. Selected bond lengths (Å) and angles (deg): Ag(1)–Ag(3), 2.8262(8); Ag(2)–Ag(3), 2.8187(8); Ag(3)–Ag(3a) 2.9623(8); Ag(1)–Ag(4), 2.8775(5); Ag(2)–Ag(5), 2.9309(6); Ag(3)–Ag(4), 3.1094(8); Ag(3)–Ag(5), 3.1249(8); H(1)–Ag(2), 1.9(2); H(1)–Ag(3), 1.75(4). (d) The $Ag_{11}(\mu_5\text{-H})$ core of the optimized structure of $[Ag_{11}(\mu_5\text{-H})\{S_2CNH_2\}]^+$ in its C_3 singlet ground state. Selected bond lengths (Å): Age–Age, 3.285; Age–Aga, 2.967; Age–Aga′, 2.969; Age–Agc, 3.191/3.166; Age–Agc′, 3.172/3.171; Aga–Agc, 3.074; Aga′–Agc', 3.074; Agc···Agc′, 3.499.

protons of propyl group is observed. The broad peak did not change its line shape but gradually shifted ~0.1 ppm upfield upon slow cooling to 210 K. This suggests the hydride rattles around the cluster. The hydride assignment was also confirmed with the corresponding deuteride complex $\mathbf{1_D}$, which displays a broad peak at 7.50 ppm in ^{2}H NMR. Finally structural elucidation of $\mathbf{1_H}$ was determined by single-crystal X-ray crystallography.‡

The geometry of the Ag_{11} skeleton in $\mathbf{1_H}$ can be best described as a hexacapped trigonal bipyramid (Fig. 1a) of which the trigonal plane is composed of three Ag3 atoms and both Ag1 and Ag2 are the axial vertices, co-linear with the C_3 axis. Both Ag4 and Ag5 (and their symmetry-generated counterparts) are the capping vertices on each side of the trigonal bipyramid. Thus an idealized D_{3h} point group symmetry is revealed in the Ag_{11} core. Ag–Ag distances along the edges of trigonal bipyramid are quite short ranging from 2.8187(8) to 2.9623(8) Å. These distances are close to the sum of the covalent radii for silver, 2.90(5) Å.[12] The Ag_{cap}–Ag_{axial} and Ag_{cap}–$Ag_{equatorial}$ distances, which are in the range of 2.9309(6)–3.1249(8) Å, are much shorter than twice of the van der Waals radius of silver, 1.7 Å.[13] Accordingly, a sketch of the eleven-vertex Ag_{11} deltahedron with degrees of vertices represented by number is exactly the same as that in Scheme 1c. It is worthwhile to note that *the degree of vertex connectivities larger than six is quite unusual in deltahedra*. Though clusters of the type, $Ag_{11}(E)(S_2CNR_2)_9$ (E = S, Se),[14] have been structurally characterized, the geometry of the Ag_{11} cage in these two compounds is approximately pentacapped trigonal prismatic. In sharp contrast, the geometry of eleven silver atoms in **1** clearly displays a hitherto unknown hexacapped trigonal bipyramid.

The Ag_{11} skeleton is further stabilized by nine dithiocarbamate ligands, giving rise to an idealized C_3 point group symmetry for the whole $[Ag_{11}(S_2CNPr_2)_9]^{2+}$ cage (Fig. 1b): three above the trigonal plane, three below, and the other three, each being connected to the capping vertices on each side of the trigonal bipyramid. Thus two distinct coordination modes for dtc ligands are observed: six quadruple bridging (μ_2, μ_2), and three terminal bridging. While Ag–S distances in the range of 2.467(2)–2.653(2) Å are observed for both Ag_{axial} and $Ag_{capping}$ atoms, slightly longer Ag–S bonds, 2.6760(19) and 2.7008(19) Å, are revealed in the $Ag_{equatorial}$ atoms.

One encapsulated hydride must reside in the $[Ag_{11}(S_2CNPr_2)_9]^{2+}$ cluster in order to balance the cluster charge. The X-ray diffraction analysis suggests that the hydride is located in one of the two tetrahedral cavities of the central trigonal bipyramid (Fig. 1c). Since unambiguous location of such a hydrogen atom by X-ray diffraction is difficult, the model $[Ag_{11}(H)\{S_2CNH_2\}_9]^+$ of C_3 symmetry was studied by DFT calculations.[15] The optimized geometry for this model system was characterized as a true minimum on the potential energy surface by frequency calculations.[16] Its $Ag_{11}H$ core with relevant distances is shown in Fig. 1d. It is rather close to D_{3h} symmetry and its computed metrical parameters are in satisfactory agreement with the corresponding X-ray data of $\mathbf{1_H}$, especially if considering that the weak d^{10}–d^{10} bonding existing between the Ag(I) centers allows the cluster cage a very large flexibility. Wiberg indices varying from 0.15 (Ag_a–Ag_b) to 0.08 (Ag_a–$Ag_{c'}$) characterize this type of bonding along the edges of the hexacapped trigonal bipyramid. The hydride is found close to the middle of the bipyramid with apical H–Ag_b and H–$Ag_{b'}$ distances differing by less than 0.02 Å. Yet, their average value (2.28 Å; corresponding Wiberg index: 0.12) is significantly longer than the equatorial H–Ag_a distances (1.90 Å; corresponding Wiberg index: 0.19). The search for another energy minimum with the hydride lying in the middle of one of the two tetrahedra constituting the trigonal bipyramid was unsuccessful. Indeed, all the trial geometries starting with the hydride lying on the C_3 axis in the middle of a tetrahedron led, after optimization, to the unique minimum shown in Fig. 1d. Such a displacement of the hydride along the C_3 axis from its equilibrium position to the center of a tetrahedron consumes approximately 0.15 eV. Moving it by only ± 0.3 Å along the C_3 axis costs less than 0.01 eV, suggesting a highly fluxional behavior at room temperature. Moreover, the displacement of the hydride into the center of one of the six capping tetrahedra constituting the hexacapped bipyramid results also, after optimization, in the unique energy minimum of Fig. 1d. Thus, there is only one equilibrium position for the hydride inside the Ag_{11} hexacapped trigonal bipyramid, *i.e.*, the center of the trigonal bipyramid. Thus, these computed data are as a whole quite consistent with the X-ray hydrogen location. The highest occupied levels of $[Ag_{11}(H)\{S_2CNH_2\}_9]^+$ are largely dominated by the participation of the sulfur lone pairs, whereas the two lowest vacant levels exhibit mostly metallic character. None of the frontier orbitals have significant hydride character. This suggests strong covalent bonding between the encapsulated

hydride and its silver cage. Consistently, the computed NBO atomic charge of H is 1.45, a value significantly lower than 2, which would correspond to pure ionic bonding.

The UV-Vis spectrum of $\mathbf{1_H}$ in CH_2Cl_2 displays two shoulder absorptions at about 419 (ε = 15800 cm^{-1} M^{-1}) and 480 (ε = 11200 cm^{-1} M^{-1}) nm, and an intense band at 275 (ε = 159800 cm^{-1} M^{-1}) nm (Fig. S2†). The origin of the high-energy band is presumably a ligand-centered transition, as the bare ligands display absorptions in the similar region.[17] Low-energy shoulder peaks could be tentatively assigned to the ligand-to-metal charge transfer transitions and are confirmed by TDDFT calculations on $[Ag_{11}(H)\{S_2CNH_2\}_9]^+$ with the two lowest transitions computed at 455 nm and 417 nm (Fig. S4†). Compound **1** exhibits red emission in both the solid state and solution upon irradiation with UV-light at 77 K. Direct excitation of the low energy band resulted in a broad, structureless emission centered at 665 nm (Fig. S2†). In degassed CH_2Cl_2 frozen glass, this peak exhibits a ~20 nm bathochromic shift towards the low-energy side of the spectrum compared to the emission at solid state. Two bands centered at 419 and 480 nm, which do correspond approximately to the low energy shoulders in the absorption spectrum, were observed from its excitation spectrum monitored at λ_{max}^{em}. The large Stokes shift (>5800 cm^{-1}) coupled with the broad, featureless emission band suggests the possibility of emission from a spin-forbidden triplet emissive state.

In conclusion, the first elemental cluster having hexacapped trigonal bipyramidal geometry is characterized in the hydride endohedral Ag_{11} cluster surrounded by nine dithiocarbamate ligands. Since the geometry of Ag_{11} cage in $Ag_{11}(E)(S_2CNR_2)_9$ (E = S, Se)[14] is that of a pentacapped trigonal prism and geometry optimization of the empty, hypothetical cluster $[Ag_{11}(S_2CNH_2)_9]^{2+}$ results in a much more open Ag_{11} polyhedron,[18] it will be of great interest to explore theoretically the role the encapsulated anions play in the cluster assembly, *e.g.* hexacapped trigonal bipyramidal and pentacapped trigonal prismatic. Work in this direction is underway.

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Notes and references

‡ Crystal data for $\mathbf{1_H}$: $C_{63}H_{127}Ag_{11}N_{10}O_3S_{18}$, M = 2836.40, T = 296(2)K, trigonal, space group $R3$, a = 20.9216(18), c = 21.233(2) Å, V = 8048.7(12) Å^3, Z = 3, ρ_c = 1.756 g cm^{-3}, μ = 2.349 mm^{-1}, $2\theta_{max}$ = 50°, R_{int} = 0.0325, R_1 = 0.0308 [$I > 2\sigma(I)$], wR_2 (all data) = 0.0787 for 8891 data (5242 independent), 311 parameters and 13 restraints. Max./min. 0.729/−0.348 e Å^{-3}. The hydride is located by the Difference Fourier synthesis and its coordinate and isotropic parameter is refined.

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